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ROYAL AIRCRAFT ESTABLISHMENT
FARNBOROUGH, HANTS

TECHNICAL NOTE No: MET.230

THE DETERMINATION OF VANADIUM IN TITANIUM ALLOYS

by

E.G.COBB. and H.J.ALLSOPP

FC

NOVEMBER,, 1955

MINISTRY OF SUPPLY, LONDON, W.C.2

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ROYAL AIRCRAFT ESTABLISHMENT, FARNBOROUGH

The Determination of Vanadium in Titanium Alloys

by

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and
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R.A.E. Ref: Mat M/11497/EGC

SUMMARY

The method describes a rapid and accurate volumetric determination of Vanadium in Titanium Alloys using an internal indicator.

The effect of various alloying constituents have been studied.

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1 Introduction

Lewis, Jepson and Brooks have described¹ the preparation and examination in the laboratory of a range of titanium-vanadium alloys in the form of 0.06" thick strip to assess their potential value as aircraft structural sheet materials. Vanadium was selected for study because it had shown promise as a strengthening agent for titanium in the early investigations of Craighead, Eastwood and Simms², also vanadium is the lightest of the metals which are known to permit stabilization of the high temperature cubic form of titanium down to room temperature. Alloys with nominal vanadium content up to 30% were examined in an initial survey and a more detailed study was made of the most promising alloy which contained 16% vanadium.

In view of this, a large number of vanadium analyses were to be expected, and therefore a quick and accurate method was required.

2 Experimental

Various methods for the determination of vanadium in titanium alloys were tried at the outset. They included (a) the gravimetric determination³ by precipitation with tannin in alkaline solution, after removal of impurities by mercury cathode electrolysis, and (b) the potentiometric titration⁴ with ferrous ammonium sulphate as titrant after an initial opening in sulphuric acid, and subsequent oxidation with ammonium persulphate.

For normal routine analysis a volumetric method was considered to be more convenient, since it would be rapid and would require no special apparatus.

In the first instance it was necessary to determine, in duplicate, 16% vanadium on sample weights not exceeding 0.3 gm. It was found unsatisfactory to employ the ferrous ammonium sulphate/potassium permanganate titration, since at this level it became necessary to use 0.02N solutions as titrants resulting in vague end-points due to masking by the vanadium colour.

Vanadium was titrated potentiometrically to obtain its oxidation/reduction potential in order to select a suitable indicator. An example of the curve obtained is shown in Fig.1. As can be seen, an indicator changing at 0.7V was required, and Diphenyl-Benzidine was found to be satisfactory. A 1% solution of this indicator in concentrated sulphuric acid was used, and providing an excess was avoided, a satisfactory end-point was obtained.

It appeared that, as with steels, the only alloying element likely to cause serious interference would be chromium. Initially this interference was removed by reduction with ferrous ammonium sulphate and the subsequent oxidation of the vanadium with potassium permanganate. However, it was found to be more satisfactory to use hydrogen peroxide, since it oxidised the titanium to the pertitanate, the vanadium to the pentavalent state and at the same time reduced the chromium⁵. The excess hydrogen peroxide was boiled off until the yellow colour of the pertitanate was discharged. Tests showed that at this stage, all the chromium was in the reduced state. An addition of potassium permanganate was then made to the cold solution to oxidise the vanadium, the excess reagent being removed by the addition of sodium nitrite in the presence of urea.

3 Recommended Method

3.1 Reagents

- 20% v/v Sulphuric Acid
- 20 volume Hydrogen Peroxide
- Approx. 0.3% Potassium Permanganate
- 0.5 gm Urea "Analoids"
- 1% aqueous Sodium Nitrite solution
- 1% Diphenylbenzidine in concentrated sulphuric acid
- 0.02N Ferrous Ammonium Sulphate
- 0.02N Potassium Dichromate

A vanadium solution of known strength, which is used to standardise the ferrous ammonium sulphate and the potassium dichromate.

3.2 Procedure

Dissolve a suitable weight of sample to contain about 20 mg vanadium (to give a titre of 20 ml ferrous ammonium sulphate), in 50 ml 20% sulphuric acid in a conical flask. When in solution add 5 ml 20 vol. hydrogen peroxide and boil until the yellow pertitanate colour is discharged. Boil a further 5 minutes, cool, and dilute to about 150 ml.

Add 0.3% potassium permanganate solution slowly until a definite pink colour persists for 5-10 minutes in the cold solution. Add 0.5 gm urea and allow to dissolve, then remove excess permanganate by the dropwise addition of 1% sodium nitrite solution. Stand 5 minutes.

To this solution add 3-4 drops of 1% diphenylbenzidine solution and stand to allow the purple colour to develop. Titrate to a green end-point with 0.02N ferrous ammonium sulphate. At first it may be found necessary to back titrate with 0.02N potassium dichromate, and then with ferrous ammonium sulphate to the correct green end-point. With practice however, a fading of the purple colour will be observed, and by careful addition of the ferrous ammonium sulphate, a definite end-point can be obtained within 1-2 drops.

A synthetic sample consisting of pure titanium and a known amount of standard vanadium, or an alloy of known vanadium content should be carried through with each batch of samples to standardise the ferrous ammonium sulphate.

4 Results

Results obtained from synthetic samples carried throughout the full procedure are given in Tables I-III(a).

The method was found satisfactory with all common alloying metals present, as well as impurities in far greater concentration than are likely to be found in the present alloys of titanium, as shown in Tables IV-VII.

5 Conclusions

By the method described it is possible to determine the vanadium content of titanium, whether in the form of sponge, powder or fabricated titanium alloys, without the use of any special apparatus.

The method is applicable to vanadium contents greater than 1 mg in the sample taken for analysis.

It is possible in many cases to carry out the titration even when the titanium has partially hydrolysed.

The presence of such alloying constituents as Iron, Manganese, Chromium, Nickel and Molybdenum and impurities such as Magnesium, Tungsten and Copper do not affect the accuracy of the method.

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| <u>No.</u> | <u>Author</u> | <u>Title, etc.</u> |
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| 3 | Payne, S.T. | "The chemical analysis of titanium and its alloys" Light Metals 17, 198, p.233 Sept. 1954 |
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Attached

Tables I to VII
Drg. Mat. 15062
Detachable Abstract Cards

Advance Distribution

PDSR(A)
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Results obtained on synthetic titanium alloysTABLE ITitanium + Vanadium

| Ti (gm) | V (gm) added | V (gm) recovered |
|---------|--------------|------------------|
| 0.2 | 0.0150 | 0.0151 |
| 0.2 | 0.0150 | 0.0150 |
| 0.2 | 0.0150 | 0.0150 |

TABLE IITitanium + Chromium

| Ti (gm) | V (gm) added | Cr (gm) added | V (gm) recovered |
|---------|--------------|---------------|------------------|
| 0.2 | nil | 0.0017 | nil |
| 0.2 | nil | 0.0017 | nil |
| 0.2 | nil | 0.0017 | nil |

TABLE IIITitanium + Vanadium + Chromium

| Ti (gm) | V (gm) added | Cr (gm) added | V (gm) recovered |
|---------|--------------|---------------|------------------|
| 0.2 | 0.0150 | 0.0017 | 0.0150 |
| 0.2 | 0.0150 | 0.0017 | 0.0150 |
| 0.2 | 0.0150 | 0.0017 | 0.0150 |

TABLE III(a)Titanium + Chromium in excess of Vanadium

| Ti (gm) | V (gm) added | Cr (gm) added | V (gm) recovered |
|---------|--------------|---------------|------------------|
| 0.2 | 0.0150 | 0.0034 | 0.01505 |
| 0.2 | 0.0150 | 0.0068 | 0.0150 |
| 0.2 | 0.0150 | 0.0102 | 0.0150 |
| 0.2 | 0.0150 | 0.0136 | 0.0151 |
| 0.2 | 0.0150 | 0.0170 | 0.01505 |
| 0.2 | 0.0150 | 0.0340 | 0.01495 |
| 0.2 | 0.0150 | 0.0850 | 0.0150 |

TABLE IV
Titanium + Vanadium + Molybdenum

| Ti (gm) | V (gm) added | Mo (gm) added | V (gm) recovered |
|---------|--------------|---------------|------------------|
| 0.2 | 0.0150 | 0.002 | 0.0149 |
| 0.2 | 0.0150 | 0.010 | 0.01495 |

TABLE V
Titanium + Vanadium + Nickel

| Ti (gm) | V (gm) added | Ni (gm) added | V (gm) recovered |
|---------|--------------|---------------|------------------|
| 0.2 | 0.0150 | 0.002 | 0.0150 |
| 0.2 | 0.0150 | 0.010 | 0.0150 |

TABLE VI
Titanium + Vanadium + Tungsten

| Ti (gm) | V (gm) added | W (gm) added | V (gm) recovered |
|---------|--------------|--------------|------------------|
| 0.2 | 0.0150 | 0.002 | 0.01495 |
| 0.2 | 0.0150 | 0.010 | 0.0149* |

* The titanium had partially hydrolysed in this sample.

TABLE VII

A synthetic alloy containing alloying constituents and impurities normally found was made up as follows:-

| | Ti | V | Cr | Ni | W | Mo | Fe | Mg | Cu | Mn |
|----------|-----|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| Wt (gms) | 1.0 | 0.030 | 0.017 | 0.010 | 0.005 | 0.010 | 0.010 | 0.005 | 0.005 | 0.010 |
| % | - | 3.0 | 1.7 | 1.0 | 0.5 | 1.0 | 1.0 | 0.5 | 0.5 | 1.0 |

Aliquots were taken to give a vanadium content of 0.0060 gm, and the following recovery was obtained:-

| | | | | | | | |
|---|---------|---|---------|---|---------|---|------------|
| 1 | 0.00599 | 2 | 0.00599 | 3 | 0.00604 | 4 | 0.00599 gm |
|---|---------|---|---------|---|---------|---|------------|

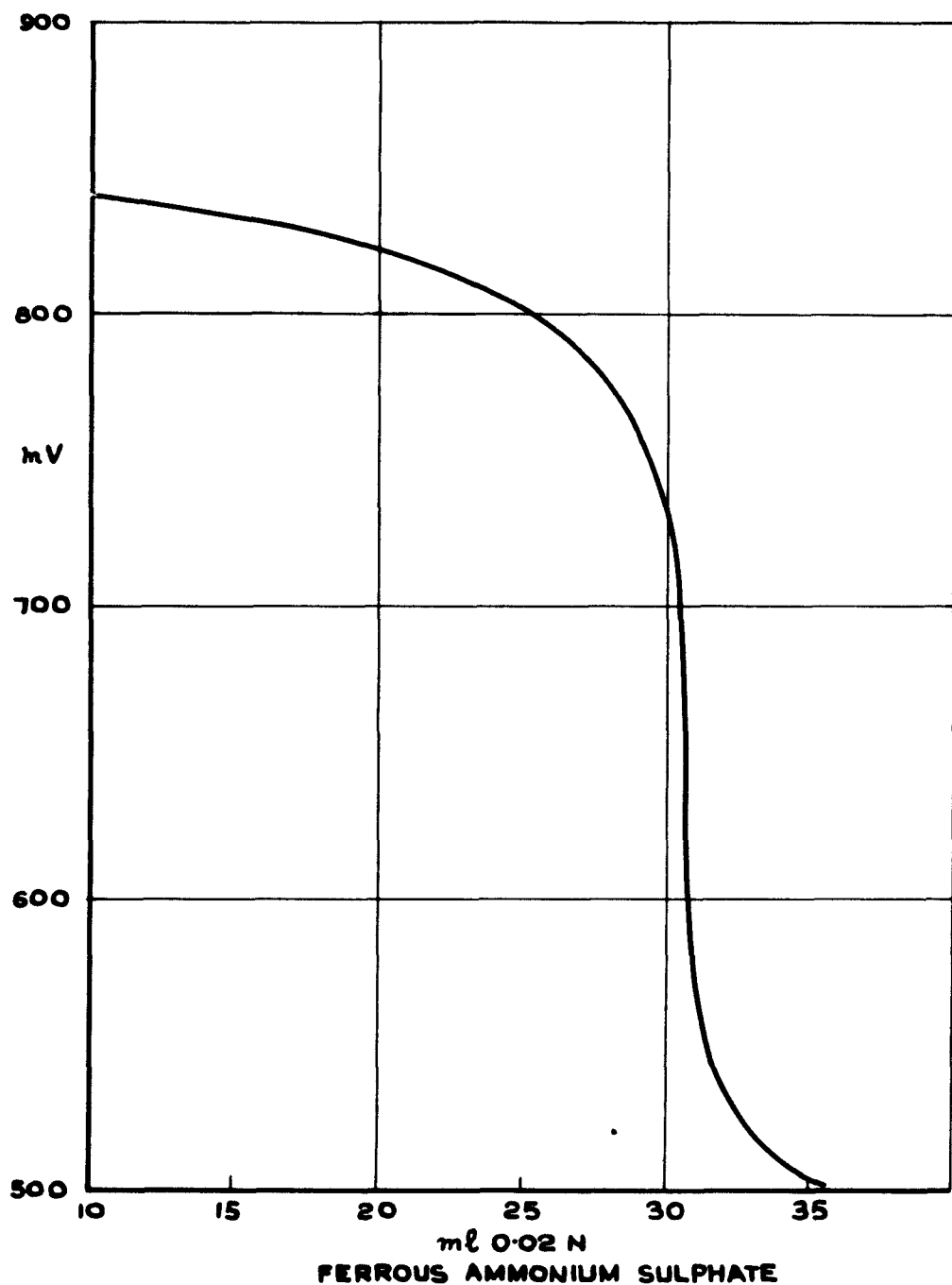


FIG. 1 - REDUCTION OF VANADATE WITH
FERROUS AMMONIUM SULPHATE



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